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OFFICE OF NAVAL RESEARCH
Contract N00014-77-C-0361
Task No. NR 319-120

STUDIES OF CONDUCTION MECHANISMS IN GAS-SENSITIVE POLYMER FILMS.

Final Report.
1 Jun 77 - 31 Aug 80

prepared by
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gas-sensitive polymers, charge-flow transistor, moisture measurement, conduction mechanism

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report documents the funding history, research highlights, and reports, publications, and patents obtained under this contract.

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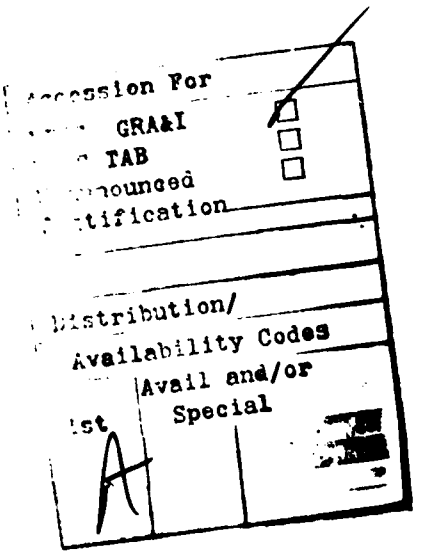
1. PROJECT DESCRIPTION.

The primary goal of this program was to understand the mechanisms of bulk and surface conduction in selected polymer films, and the effects of adsorbed species on these conduction mechanisms.

A second goal was to develop and exploit a novel technique for studying such conduction mechanisms based on a new microelectronic device called the charge-flow transistor.

A third goal was generally to develop charge-flow transistor technology as a measurement technique for studying adsorbed species and for other applications.



II. FUNDING HISTORY.

This contract had three funding periods, as follows:

1 Jun 77 - 30 April 78 -- $35,000.

1 May 78 - 30 April 79 -- $35,000.

1 May 79 - 30 April 80 -- $35,000, subsequently extended to 31 August 80 at no additional cost.

Total funding over 39 months -- $105,000.

III. RESEARCH HIGHLIGHTS.

The first major research result was the quantitative identification of threshold voltage and transconductance shifts in charge-flow transistors coated with films of poly p-aminophenylacetylene (abbreviated PAPA) of varying thicknesses. These shifts were attributed to a shift of the charge centroid of the injected charge away from the polymer-oxide interface toward the surface of the polymer film. The presence of these shifts had both beneficial and detrimental effects: one the one hand, their presence enabled studies of the relative roles of bulk and surface conduction in the polymer film; on the other hand, the threshold voltage shifts greatly complicated the quantitative extraction of conductivity information from the data. This phase of the work is summarized in the thesis of Huberman (Reference 1. References are collected in Section IV below).

In spite of the difficulties in making precise quantitative interpretations of device characteristics, it was discovered that charge-flow transistors coated with PAPA had turn-on times that varied enormously with ambient moisture, a fact that correlated well with independent observations of the variation of sheet conductance with moisture. Variations of turn-on time over more than five decades were observed. These results were reported at two conferences, as cited in References 2 and 3.

During the measurements of turn-on time, it was noted that surface currents flowing across the device could modify the device characteristics, which led to the discovery of a modified device metallization scheme with improved performance. A patent on this invention was recently issued (Reference 4).

Also during the turn-on time studies, it was noted that the large variations of turn-on times (from milliseconds to thousands of seconds, depending on moisture) required the development of new measurement techniques. A new type of circuit, called the charge-flow transistor oscillator, was invented and patented (Reference 5). This oscillator, the first discrete version of which was published in Reference 6, made possible the development of fully integrated moisture sensing devices, as described at the 1978 Device Research Conference (Reference 7).

Work on the fundamental conduction mechanism in PAPA was continued by Bowen (Reference 8). It was discovered that the threshold voltage and transconductance shifts observed previously were actually manifestations of slow transients in the device's approach to steady-state conditions. By making studies of both the temperature and moisture dependence of the conductivity of PAPA films, it was determined that there are two primary moisture-related conduction mechanisms, one at low temperature (below 40 C) which has the same activation energy as protons in water, and a second at

higher temperaturee (above 40 C) which has the same activation energy as conduction in pressed powder samples of PAPA, suggesting conduction involving the amino protons on the polymer. Both mechanisms have the same moisture dependence, identifying the origin of the moisture-related conductivity as ionic, and very likely protonic. The threshold voltage and transconductance shifts could then be identified as involving bulk ionic conductivity, and the disappearance of these shifts at long time as due to weak bonding of ionic species to the oxide interface. A report of this work for publication is in draft.

The final phase of work, during the extension period into the summer of 1980, involved the design and construction of a vastly improved moisture generating system which is capable of reaching dew points down to -60 C, and the testing of some new polymeric materials that involve copolymers of polyethylene oxide and polypropylene oxide in combination with an improved device structure with which sheet conductance measurements can be made quantitatively. The effect of film thickness and polymer composition can be observed, but further work is needed before these results will be ready for publication.

IV. REPORTS, PUBLICATIONS, AND PATENTS.

A total of eight Technical Reports publications, patents, and conference papers were produced under this program. They are listed below in approximate chronological order:

1. M. G. Huberman, "Surface and Bulk Conduction Studies with the Charge-Flow Transistor", S.M. Thesis, Massachusetts Institute of Technology, September, 1977; issued as Technical Report No. 1.

2. S. D. Senturia, M. G. Huberman, and R. Van der Kloot, "Moisture Sensing with the Charge-Flow Transistor", Proc. ARPA/NBS Workshop on Moisture in Integrated Circuit Packages, Gaithersburg, MD, March 1978.

3. S. D. Senturia, M. G. Huberman, and R. Van der Kloot, "Study of Thin-Film Conduction Using the Charge-Flow Transistor", contributed paper at the April Meeting of the American Physical Society; abstract published in Bull. Am. Phys. Soc. 23, 328 (1978).

4. S. D. Senturia, "Charge-Flow Transistors Having Metallization Patterns", U.S. Patent 4,209,796 issued June 24, 1980, assigned to the Massachusetts Institute of Technology. The Government has rights in this invention pursuant to this contract (N0014-77-C-0361).

5. S. D. Senturia, "Oscillators Including Charge-Flow Transistor Logic Elements", U.S. Patent 4,236,121 issued Nov. 25, 1980, assigned to the Massachusetts Institute of Technology. The Government has rights in this invention pursuant to this contract (N0014-77-C-0361).

6. S. D. Senturia and M. T. Fertsch, "A Charge-Flow Transistor Oscillator Circuit", J. Solid State Circuits, SC-14, 753 (1979).

7. S. D. Senturia, M. G. Huberman, and R. Van der Kloot, "An Integrated Humidity Sensor Based on the Charge-Flow Transistor", paper presented at the IEEE Device Research Conference, Santa Barbara, CA, June 1978; abstract published in IEEE Trans. Electron Devices 25, 1351 (1978).

8. N. L. Bowen, "The Study of the Electrical Conductivity of Poly (p-aminophenylacetylene) Using Charge-Flow Devices", S.M. Thesis, Massachusetts Institute of Technology, October 1979; issued as Technical Report No. 2.